

Crystal Structure of Cupric Di-L-ornithinate Dichloride Dihydrate

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The crystal structure of cupric di-L-ornithinate dichloride dihydrate, $\text{Cu}[\text{HN}_3(\text{CH}_2)_3\text{CH}(\text{NH}_2)\text{COO}]_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, has been determined using three-dimensional intensity data. The crystal data are $a=5.18$, $b=15.57$, $c=11.90$ Å, $\beta=93.3^\circ$, space group $P2_1/c$; there are two molecules in the cell. The structure has been refined by the full-matrix least-squares method. The final R is 0.087. The molecule shows a distorted octahedral geometry around copper, with two pairs of oxygen and nitrogen atoms forming an approximately square planar coordination, while the two chloride ions are at the apical positions. All the hydrogen atoms available for hydrogen bond formation are satisfied.

Introduction

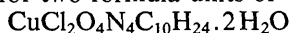
The function of amino acid L-ornithine in the living system is very important. In the present paper the crystal and molecular structure of a copper complex of L-ornithine chloride, namely cupric diornithinate dichloride dihydrate having the chemical formula $\text{Cu}[\text{NH}_3(\text{CH}_2)_3\text{CH}(\text{NH}_2)\text{COO}]_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ is reported.

Experimental

Cupric diornithinate dichloride (Taurins, 1950) crystallizes as thin plates, elongated along the a axis, when an aqueous solution is evaporated slowly. The crystal is deep blue in colour and is stable at room temperature. It is also unaffected by humidity.

Unit-cell dimensions and space group

Rotation and Weissenberg photographs taken about the needle axis showed that the crystal belongs to the monoclinic system. The unit-cell dimensions are $a=5.18$, $b=15.57$, $c=11.90$ Å, $\beta=93.3^\circ$. The only systematic absences were for $0k0$ with k odd and $h0l$ with l odd. But, a few of the $h0l$ reflexions with l odd had observable intensities. These forbidden spots were in fact the Renninger (1937) reflexions of the incident beam by two sets of strong planes, as found from a study of the reflecting conditions of the reciprocal lattice (Table 1). The space group therefore is $P2_1/c$. The density of the crystal determined by the flotation method was found to be 1.501 g.cm $^{-3}$, while the calculated value for two formula units of



in the unit cell was 1.506 g.cm $^{-3}$. The molecule was therefore centrosymmetric with the copper atom at the origin.

Intensity measurement

Data up to the fourth layer along the needle axis a were collected from Weissenberg photographs using

the equi-inclination technique with $\text{Cu K}\alpha$ radiation. The intensities were estimated visually with standard calibrated strips. The intensity value assigned to the unobserved reflexions, *i.e.* reflexions with intensities too weak to be observed, was one half the minimum value that it had been possible to observe. The intensity values for different layers were corrected for spot size (Phillips, 1954, 1956) and for Lorentz and polarization factors. As the crystal used was very thin, about 0.03 mm on each side of the cross section, no absorption correction was necessary for the data collected along the needle axis, the linear absorption coefficient being 45.0 cm $^{-1}$.

The crystals being very thin there was a lot of practical difficulty in cutting them to proper shape and size for taking photographs about other axes. A zero layer line photograph was, however, taken about the b axis with the idea of putting the intensities on the same relative scale by a cross-layer correlation method, but this was not successful, owing to the irregular absorption of the crystal used. The intensities of each of the five layer line photographs about the a axis were then separately placed on an absolute scale by Wilson's statistical method.

Structure determination

A three-dimensional point atom sharpened Patterson synthesis using all the reflexions was then computed. The Cu-Cu, Cu-Cl and Cl-Cl interaction vectors were identified from this synthesis. The structure factors were calculated for all the reflexions with the coordinates of copper and chlorine atoms obtained. The disagreement factor R was 0.45.

A three-dimensional Fourier synthesis was then calculated using the signs of the copper and chlorine atoms. About 65% of the reflexions to which signs could be assigned confidently were used. A spoke and bead model was constructed with the electron density peaks obtained from this synthesis. This model helped in deriving the structure completely. The proposed structure was satisfactory from stereochemical considerations. The R value for all the atoms was 0.26.

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Refinement of the structure

The three-dimensional refinement of the structure was then undertaken by the method of least-squares. To start with, three cycles of full-matrix least-squares refinement using isotropic temperature factors was made on a 32 K core memory CDC 3600 computer at the Tata Institute of Fundamental Research, Bombay. The program used was the modified version of the *ORFLS* program of Busing, Martin & Levy (1962). The function minimized in the least-squares calculation was the sum of the squares of the differences between the observed and calculated structure factors, *i.e.* $w(F_o - F_c)^2$, where the summation was over all reflexions and w the weighting factor. A plot of $w(\Delta|F|)^2$ as a function of $(\sin \theta/\lambda)$ and $|F_o|$ did not suggest any obvious weighting scheme. Each reflexion was, therefore, given a unit weight. The unobserved reflexions, however, were excluded from initial stages of refinement. The scale factors for the five layers were also subjected to refinement so that the error due to interlayer scaling might be minimized. The scattering factors for C, N, O, Cl⁻ and Cu atoms were taken from *International Tables for X-ray Crystallography* (1960). The *R* value decreased to 0.141. Next, two more cycles of full-matrix least-squares refinement using anisotropic temperature factors were carried out and *R* was found to decrease to 0.095.

A three-dimensional difference Fourier synthesis was then calculated with all the reflexions. This synthesis

did not show any peak with density exceeding ± 0.3 e.Å⁻³. The hydrogen atoms, however, could not be located unequivocally.

After two more cycles of full-matrix anisotropic least-squares refinement the *R* value for 1487 observed reflexions converged to 0.0869 and 0.0908 when 106 unobserved reflexions were included. The shifts in the parameters in the final cycle were much less than their estimated standard deviations.

The positional and thermal parameters of the atoms together with their estimated standard deviations are given in Tables 2(a) and (b) respectively. The observed and calculated structure factors are given in Table 3. The composite drawing of the final Fourier synthesis is shown in Fig. 1.

Discussion of the structure

Intramolecular characteristics

The dimensions of the molecule are shown in Fig. 2. The molecular packing viewed along *c* and *a* axes is shown in Figs. 3 and 4 respectively. The intramolecular and intermolecular bond angles and bond distances are given in Table 4 and 5 respectively.

The crystal structure of the copper ornithine complex, Cu(L-orn)₂Cl₂·2H₂O, is similar in many ways to those of other Cu(II) complexes of amino acids whose crystal structures have already been determined. The α -amino nitrogen and a carboxyl oxygen in each of the two centrosymmetrically related bidentate orni-

Table 1. *Renninger reflexions*

Observed forbidden reflexions	Pairs of planes giving rise to the corresponding forbidden reflexion
0 0 3	2 3 8. $\bar{2}$ $\bar{3}$ $\bar{8}$
0 0 5	1 2 8. $\bar{1}$ $\bar{2}$ $\bar{8}$
0 0 7	1 8 4. $\bar{1}$ $\bar{8}$ 3; 0 4 2. 0 $\bar{4}$ 5
$\bar{1}$ 0 3	$\bar{1}$ 3 4. 0 $\bar{3}$ $\bar{1}$; $\bar{1}$ 4 6. 0 $\bar{4}$ $\bar{3}$; $\bar{1}$ 2 9. 0 $\bar{2}$ $\bar{6}$; 0 8 7. $\bar{1}$ $\bar{8}$ $\bar{4}$
$\bar{1}$ 0 5	1 8 9. $\bar{2}$ $\bar{8}$ $\bar{4}$
$\bar{2}$ 0 5	2 6 1. $\bar{4}$ $\bar{6}$ 4; 2 9 10. $\bar{4}$ $\bar{9}$ $\bar{5}$
3 0 3	0 5 1. 3 $\bar{5}$ 2
$\bar{3}$ 0 3	0 7 2. $\bar{3}$ $\bar{7}$ 1
$\bar{3}$ 0 5	$\bar{2}$ 2 2. $\bar{1}$ $\bar{2}$ 3; 0 5 1. $\bar{3}$ $\bar{5}$ 4; 0 7 2. $\bar{3}$ $\bar{7}$ 3
$\bar{4}$ 0 1	0 4 12. $\bar{4}$ $\bar{4}$ $\bar{11}$

Table 2(a). *The positional parameters of the atoms and their standard deviations*

	<i>x/a</i>	$\sigma(x)$	<i>y/b</i>	$\sigma(y)$	<i>z/c</i>	$\sigma(z)$
Cu	0.0000		0.0000		0.0000	
Cl	-0.2608	0.0021 Å	-0.3491	0.0020 Å	-0.4216	0.0019 Å
O(W)	0.7678	0.0081	-0.3453	0.0075	0.0046	0.0065
N(2)	0.4700	0.0069	-0.3920	0.0067	-0.1888	0.0064
C(5)	0.2381	0.0105	-0.3351	0.0125	-0.1959	0.0113
C(4)	0.3131	0.0110	-0.2416	0.0115	-0.2079	0.0112
C(3)	0.0660	0.0120	-0.1882	0.0126	-0.2026	0.0130
C(2)	0.1146	0.0097	-0.0915	0.0100	-0.1943	0.0093
N(1)	0.2420	0.0060	-0.0732	0.0061	-0.0822	0.0060
O(2)	-0.2401	0.0070	-0.0480	0.0064	-0.3132	0.0060
C(1)	-0.1474	0.0087	-0.0472	0.0089	-0.2132	0.0094
O(1)	-0.2277	0.0052	0.0020	0.0058	-0.1390	0.0052

Table 2(b). The anisotropic temperature factors of the atoms and their standard deviations

	β_{11}	(σ_{11})	β_{22}	(σ_{22})	β_{33}	(σ_{33})	β_{12}	(σ_{12})	β_{13}	(σ_{13})	β_{23}	(σ_{23})
Cu	0.02967	0.00045	0.00349	0.00004	0.00595	0.00006	0.00037	0.00009	0.00066	0.00011	0.00005	0.00003
Cl	0.02449	0.00115	0.00330	0.00009	0.00500	0.00014	0.00003	0.00020	0.00171	0.00025	0.00006	0.00009
O(W)	0.06175	0.00411	0.00504	0.00037	0.00592	0.00051	-0.00022	0.00097	-0.00124	0.00111	0.00001	0.00035
N(2)	0.02485	0.00323	0.00303	0.00030	0.00547	0.00049	-0.00013	0.00070	0.00144	0.00089	0.00040	0.00031
C(5)	0.02408	0.00470	0.00700	0.00067	0.01049	0.00099	0.00323	0.00129	0.00339	0.00152	0.00325	0.00066
C(4)	0.10851	0.00893	0.00404	0.00055	0.00819	0.00091	0.01409	0.00180	-0.01652	0.00231	0.00373	0.00060
C(3)	0.05198	0.00642	0.00515	0.00059	0.01687	0.00169	0.00019	0.00148	-0.00204	0.00245	0.00073	0.00079
C(2)	0.03304	0.00454	0.00484	0.00048	0.00693	0.00072	0.00457	0.00106	-0.00353	0.00128	0.00230	0.00046
N(1)	0.02378	0.00299	0.00247	0.00026	0.00398	0.00044	0.00046	0.00064	-0.00084	0.00082	0.00103	0.00028
O(2)	0.05185	0.00354	0.00383	0.00030	0.00548	0.00044	0.00490	0.00079	-0.00108	0.00096	0.00123	0.00027
C(1)	0.01885	0.00396	0.00341	0.00039	0.00848	0.00078	0.00309	0.00088	0.00303	0.00122	0.00040	0.00044
O(1)	0.01972	0.00249	0.00386	0.00027	0.00501	0.00040	-0.00052	0.00059	0.00072	0.00072	0.00042	0.00027

thine ligands are linked to copper and form almost a square planar configuration. The Cu(II)-N(I) and Cu(II)-O(I) distances have been found to be 1.992 ± 0.006 and 1.976 ± 0.005 Å, respectively, while the average values for these distances, as compiled from similar other complexes (Freeman, 1967) are 2.00 ± 0.005 and 1.98 ± 0.012 Å, respectively. The values for the ligand-Cu-ligand angle in copper complexes of different amino acids show that this angle in the coordination square is very sensitive to environments. This angle in $\text{Cu(L-orn)}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ is $87.74 \pm 0.23^\circ$. There are two chloride ions bonded axially to the Cu(II) atom, the length of the bond being 2.891 ± 0.002 Å. This Cu-Cl bond makes an angle of 72.8° with the plane of the coordination square, thus presenting the picture of a distorted octahedron.

Although it was expected that owing to the central metal atom forming the chelate ring the C(1)-O(1) and C(1)-O(2) distances would be different, they were in the present case found to be equal (1.257 ± 0.011 Å). The carboxyl group in $\text{Cu(L-orn)}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ is approximately planar. The equation of the least-squares plane

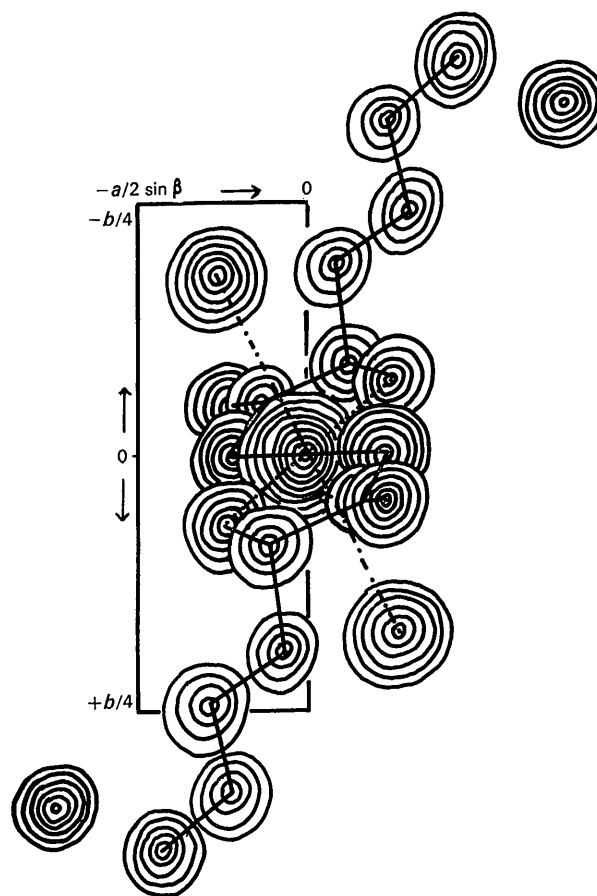


Fig. 1. Composite three-dimensional final electron-density map projected along c axis. Contours are at intervals of $2 \text{ e.}\text{\AA}^{-3}$ starting from $1 \text{ e.}\text{\AA}^{-3}$ for C, N and O atoms and at intervals of $4 \text{ e.}\text{\AA}^{-3}$ starting from $2 \text{ e.}\text{\AA}^{-3}$ for Cl^- and Cu atoms.

Table 3. The observed and calculated structure factors

Within each group the columns, reading from left to right, contain the values I, 10F_o and 10F_c. The unobserved reflexions are not included.

Table with multiple columns of numerical data representing structure factors. The columns are grouped by h, k, l indices. Each group contains observed intensity (I), observed structure factor (10F_o), and calculated structure factor (10F_c). The table is organized into several distinct sections based on the h, k, l values.

Table 3 (cont.)

3	35	45	5	85	-74
4	24	30	6	45	31
5	124	127	7	26	78
6	16	-34	8	40	55
7	183	190			
8	35	-17			
			$h = 4, k = 13$		
			0	20	-11
			1	197	201
			2	16	-10
			3	89	73
			4	14	8
			5	142	100
			6	47	-36
			$h = 4, k = 11$		
			1	65	97
			2	19	-33
			3	76	86
			4	69	-79
			5	97	86
			6	70	-61
			7	114	124
			$h = 4, k = 11$		
			1	197	189
			2	19	-33
			3	63	75
			4	79	-97
			5	79	73
			6	45	-30
			7	164	189
			8	126	120
			9	41	51
			0	50	62
			$h = 4, k = 12$		
			0	27	40
			1	85	94
			2	108	103
			3	51	-93
			4	31	44
			5	85	-54
			$h = 4, k = 12$		
			1	80	-52
			2	86	101
			3	54	-60
			4	67	80
			$h = 4, k = 14$		
			0	37	19
			1	44	-32

passing through the atoms C(2), C(1), O(1) and O(2) is

$$-0.5377x' - 0.8204y' + 0.1965z' = 0.4722$$

where x' , y' , z' are coordinates in ångströms referred to a set of orthogonal axes given by $x' = x \sin \beta$, $y' = y$, $z' = z + x \cos \beta$. The deviations of the atoms

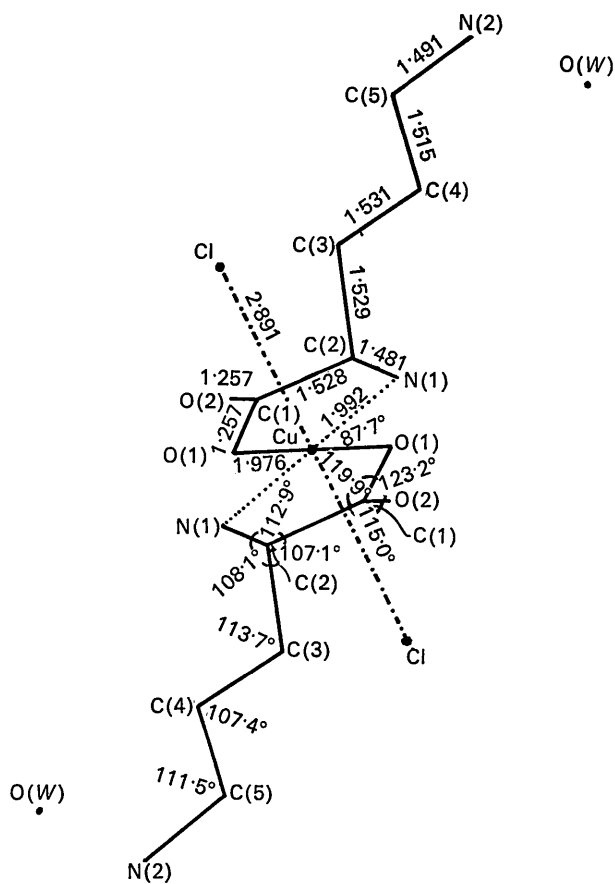


Fig. 2. Bond lengths and bond angles

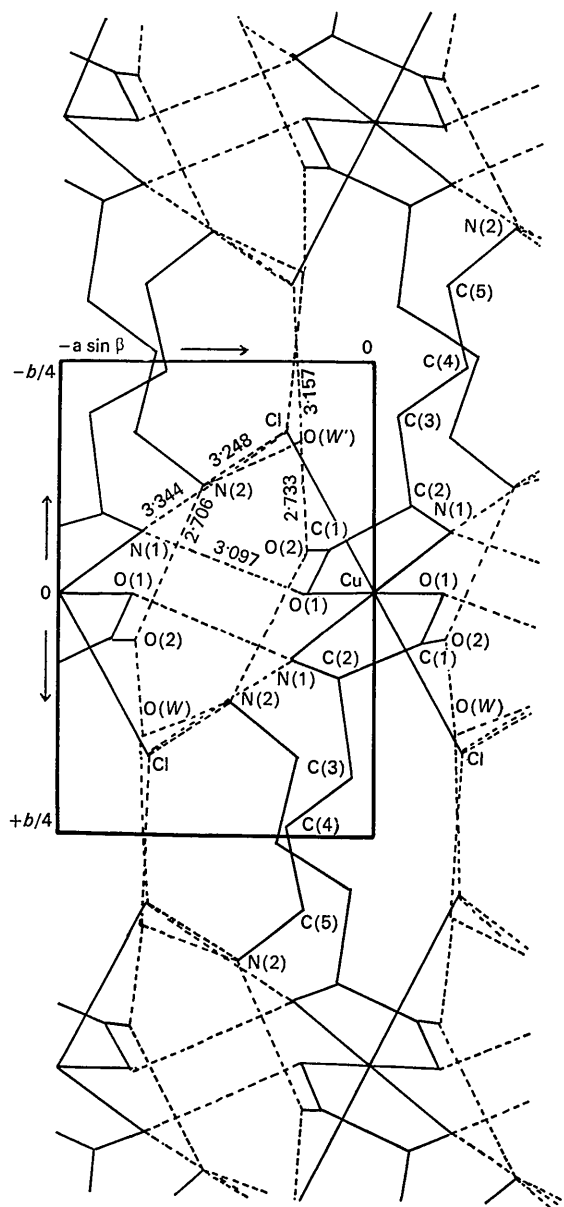


Fig. 3. Molecular packing viewed along c axis. The dashed lines indicate hydrogen bonds.

C(1), C(2), O(1), O(2), N(1) and Cu from this plane are $+0.051$, -0.083 , -0.176 , $+0.090$, -0.416 and -0.472 Å respectively.

None of the bond distances or angles in the ornithine residue differs significantly from those of other metal amino acid complexes (Freeman, 1967). Their values do not differ significantly from those obtained in the unchelated molecule L-ornithine.HCl (Chiba, Ueki, Ashida, Sasada & Kakudo, 1967; Guha, Mazumdar & Saha, 1969). The conformations of the chelated amino acid and the hydrochloride, however, do differ. For example, the carboxyl group in the hydrochloride is much more planar and the deviations of N(1) from the plane is considerably greater.

Table 4. *Intramolecular interatomic distances and angles*

Bond distance		Bond angle	
Cu—O(1)	1.976 ± 0.005 Å	O(1)—C(1)—O(2)	123.2 ± 0.6°
Cu—N(1)	1.992 ± 0.006	O(1)—C(1)—C(2)	119.9 ± 0.8
Cu—Cl	2.891 ± 0.002	O(2)—C(1)—C(2)	115.0 ± 0.8
C(1)—O(1)	1.257 ± 0.011		
C(1)—O(2)	1.257 ± 0.011	N(1)—C(2)—C(1)	112.9 ± 0.7
C(1)—C(2)	1.528 ± 0.013	C(3)—C(2)—C(1)	107.1 ± 0.8
C(2)—N(1)	1.481 ± 0.011	C(3)—C(2)—N(1)	108.1 ± 0.8
C(2)—C(3)	1.529 ± 0.016	C(4)—C(3)—C(2)	113.7 ± 1.0
C(3)—C(4)	1.531 ± 0.017	C(5)—C(4)—C(3)	107.4 ± 0.9
C(4)—C(5)	1.515 ± 0.017	N(2)—C(5)—C(4)	111.5 ± 0.9
C(5)—N(2)	1.491 ± 0.013		

Table 5. *Intermolecular bond distances and bond angles hydrogen bonding*

Donor—H...Acceptor	Bond distance	Carbon—donor...Acceptor	Bond angle
N(1)—H...O(1)*1	3.097 ± 0.008 Å	C(2)—N(1)...O(1)*1	103.4 ± 0.5°
N(1)—H...Cl*2	3.344 ± 0.006	C(2)—N(1)...Cl*2	137.2 ± 0.5
N(2)—H...O(W)	2.792 ± 0.009	C(5)—N(2)...O(W)	107.4 ± 0.5
N(2)—H...O(2)*3	2.706 ± 0.009	C(5)—N(2)...O(2)*3	100.4 ± 0.5
N(2)—H...Cl*1	3.248 ± 0.006	C(5)—N(2)...Cl*1	95.0 ± 0.5
O(W)—H...Cl*2	3.157 ± 0.008		
O(W)—H...O(2)*2	2.733 ± 0.009		
Close nonbonded contact			
N(2)...O(1)*3	2.860 ± 0.008 Å	C(5)—N(2)...O(1)*3	150.4 ± 0.5°
	*1: 1 + x, y, z		
	*2: 1 + x, -½ - y, ½ + z		
	*3: -x, -½ + y, -½ - z		

Intermolecular characteristics

Of the two amino groups in each ornithinate residue, it is known that the terminal amino group is more basic than the α -amino group. So, in the solid state it is expected that the Cl⁻ ion would be associated with the terminal amino nitrogen through hydrogen bond. In cupric diornithinate dichloride dihydrate both the α -amino and the terminal amino groups form hydrogen bonds with Cl⁻ ion. It may, however, be noted that the hydrogen bond with Cl⁻ formed by the terminal nitrogen (3.248 Å) is stronger than that formed by α -amino nitrogen (3.344 Å).

The α -amino nitrogen and the terminal amino nitrogen atoms have altogether five hydrogen atoms available for bond formation: two from α -amino N(1) of the C(2)—N(1)H₂ group and three from the terminal amino nitrogen N(2) of the C(5)—N(2)H₃ group. The —N(1)H₂ group has the expected two close neighbours but the C(5)—N(2)H₃ group has four, all of them being within the range of hydrogen bonding distances. It may be noted that both the α - and terminal-amino nitrogen atoms N(1) and N(2) should assume tetrahedral configuration, *i.e.* the C—N...X angles should not be far away from the tetrahedral values. This condition is not satisfied by the angle C(5)—N(2)...O(1)*3 = 150.4°. It is, therefore, concluded that this site is not involved in hydrogen bond formation.

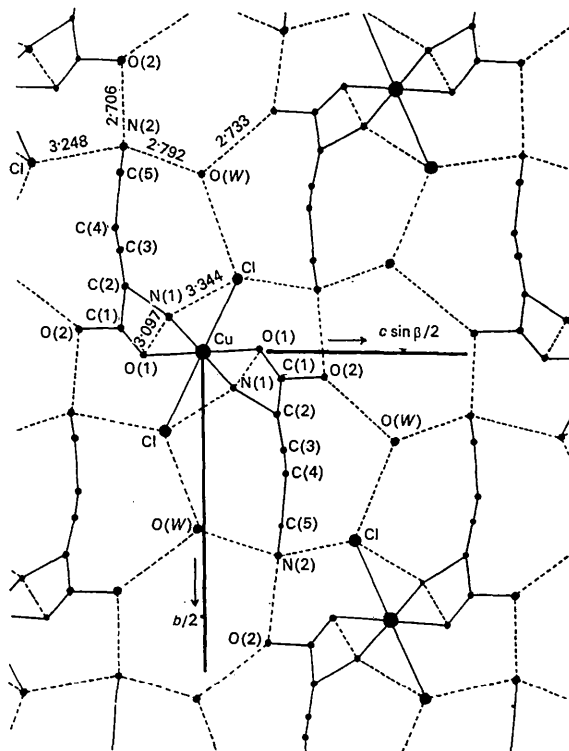


Fig. 4. Molecular packing viewed along *a* axis. The dashed lines indicate hydrogen bonds.

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An Investigation of the Crystal Structure of Mn_5Ge_3 Using Single-Crystal Neutron Time-of-Flight Techniques

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The Harwell electron linear accelerator has been used to provide a pulsed source of thermal neutrons. The intensities of many diffraction peaks from a single crystal of Mn_5Ge_3 were measured simultaneously by a time of flight technique. The various corrections to this data are described and the set of structure factors derived is compared with a calculated set. The time of flight technique using a pulsed white beam of thermal neutrons provides structure factors at several wavelengths thus giving an immediate indication of the magnitude of the extinction effect. For the majority of reflexions measured in this experiment extinction effects cannot be neglected for measurements made at wavelengths greater than 0.5 Å. After approximate correction for these effects optimum values for the two positional parameters in the $D8_8$ structure are found.

Introduction

When determining the structure of a complex molecule by diffraction techniques it is difficult to resolve sufficient lines from a powder sample so one is normally forced to use a single crystal. X-ray diffraction is the quickest and cheapest method of structure factor determination but in certain cases the distinct advantages of neutron diffraction (Bacon, 1955) are indispensable. However, intense neutron sources (reactors and others) are expensive and it is important to make maximum use of the available time. For this reason it is desirable to improve the rates of data collection using existing neutron sources and to be ready to use the next generation of intense sources which is likely to consist mainly of pulsed reactors (Brugger, 1968).

What we will call the conventional technique is shown in Fig. 1(a). A monochromatic (mono-energetic) beam of neutrons is selected from a well collimated beam of thermal neutrons by Bragg reflexion from a large single crystal and the small specimen crystal is set so that each plane in turn reflects this beam on to a detector. The measurement of the intensity of each peak involves an (ω , 2θ) scan over some few degrees.

In the time-of-flight technique (Buras, Mikke, Lebeck & Leciejewicz, 1965; Lowde, 1956) a pulsed white beam of neutrons falls on the specimen and the diffracted neutrons are analysed as a function of direction and time of flight and hence wavelength [Fig. 1(b)]. Thus with a large enough array of detectors the intensities of reflexions above some minimum wavelength (and hence below some maximum Miller indices) can be determined.

Comparisons are difficult to make but we have shown (Day & Sinclair, 1968) that a one kilowatt pulsed neutron source based on a rather low-powered electron linear accelerator (linac) can give comparable results to the conventional technique on a fairly high flux (15 MW) reactor, and that the use of a chopped beam on that reactor would show a considerable gain over the conventional technique. When intense pulsed neutron sources become available time of flight techniques seem to be the only logical approach to achieving the potential gain in rates of data acquisition.

However, there are obviously many questions to be answered and many difficulties to be overcome before the crystallographer can be expected to welcome these techniques. This paper aims to show that many of these